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Phase behavior in copolymer blends of polystyrene and poly(*o*-chlorostyrene-co-*p*-chlorostyrene)

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The miscibility of random copolymers of *o*-chlorostyrene and *p*-chlorostyrene [P(*o*ClS-*p*ClS)] with polystyrene (PS) has been studied by differential scanning calorimetry (DSC). A miscibility "window" was found, extending in copolymer composition from about 68 to 98 mole % *o*-chlorostyrene at a temperature of 150 °C. The maximum in the miscibility window occurred at approximately 170 °C and a composition of 83 mole % *o*-chlorostyrene. This result differs only slightly from theoretical predictions based on interaction parameters previously calculated from miscibility behavior in blends of poly(2,6-dimethyl-1,4-phenylene oxide) with P(*o*ClS-*p*ClS), poly(styrene-co-*o*-chlorostyrene) and poly(styrene-co-*p*-chlorostyrene). The implication of this result for the numerical values of the six interaction parameters required to describe these blends is discussed.

INTRODUCTION

The phase behavior of blends containing a random copolymer has recently been the subject of extensive investigations, theoretically[1–3] as well as experimentally.[4–9] One of the principal conclusions is the possibility of a miscibility "window" arising from a "repulsion" effect. This refers to a situation where the positive value of the segmental interaction parameter χ of the two monomers constituting the random copolymer is sufficiently large to overcome the positive values of the two other χ parameters involved. As a result miscibility can be found for a certain range of copolymer compositions even though none of the three homopolymers derived from the respective monomers are mutually miscible. The regime of miscibility in the temperature-copolymer composition plane is separated from the immiscibility regime by a boundary delineating the loci of lower critical solution temperatures (LCSTs) for the respective systems. High-temperature phase separation with concommitant LCSTs arises as a result of the destabilizing effect of the compressibility in polymer-polymer systems.[2,10,11]

In a previous publication[2] the miscibility of blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with P(*o*ClS-*p*ClS), poly(styrene-co-*o*-chlorostyrene) [P(S-*o*ClS)] and poly(styrene-co-*p*-chlorostyrene) [P(S-*p*ClS)] was discussed. At any given temperature between 200 and 280 °C there are in these three systems four blends, characterized by the respective copolymer compositions, which have a LCST at that temperature. In this way four independent equations were obtained containing the six χ parameters characterizing these systems. The values of these interaction parameters at 200 °C were calculated assuming in addition a value of -0.1 for the χ parameter describing the interaction of PPO and PS, and a value of 0.005 for the χ parameter for the PS and poly(*o*-chlorostyrene)[2] pair. These latter values were estimated from additional information which was available for these systems. We pointed out that all six interaction parameters could in principle also be calculated as a function of temperature from the determination of miscibility boundaries alone (e.g., by DSC) provided that a miscibility window existed for the PS-P(*o*ClS-*p*ClS) system in the appropriate temperature range ($T > 200$ °C). This would provide the required two further independent equations. On the basis of the calculated values of the χ parameters[2] we estimated that the latter system should in fact display a miscibility window extending in copolymer composition from about 55 to 95 mole % *o*-ClS at a temperature of 200 °C. Assuming an approximately symmetric miscibility window, as is the case for the other systems,[4,7–9] the maximum was predicted to occur at a copolymer composition of about 75 mole % *o*ClS.

In this paper we present the results for PS/P(*o*ClS-*p*ClS) blends which were studied to examine these predictions. The predicted miscibility window was found; it extended in copolymer composition from 68 to 98 mole % *o*ClS at 150 °C. The maximum occurred at a temperature of 170 °C for the copolymer containing 83 mole % *o*ClS. This is reasonably close to the theoretical predictions; however the data does not yet enable us to calculate the temperature dependence of the interaction parameters, because the miscibility windows in the blends involving PPO could only be determined for temperatures above 200 °C, due to the relatively high T_g of PPO ($\approx$210 °C).

Some of the consequences of these results with respect to the numerical values of the χ parameters can nevertheless be evaluated. To that end we consider that for a somewhat lower molecular weight of PS or P(*o*ClS-*p*ClS) the PS/P(*o*ClS-*p*ClS) system will extend its miscibility window to yield a maximum near 200 °C at approximately 83 mole % *o*ClS. This is a reasonable assumption since theoretically a

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change in molecular weight of either component will not influence the copolymer composition corresponding to the maximum in the miscibility window.

It will be shown that the combined available information readily determines the relative magnitudes and signs of the interaction parameters with considerable precision. However, some additional input is necessary to obtain absolute values.

EXPERIMENTAL SECTION

Copolymers

All copolymers were prepared by free radical polymerization in toluene. In this way a high molecular weight product of atactic structure and a degree of polydispersity of about 2 was obtained. The polymerization was stopped at a conversion of 60% to prevent copolymer composition drift. Molecular weights were obtained by gel permeation chromatography (GPC) at 25 °C in tetrahydrofuran (THF). The copolymer compositions were determined by infrared and ^{13}C nuclear magnetic resonance (NMR) analysis. Table I presents the relevant data for the copolymers used in this study.

Polystyrene

Polystyrene, obtained from Pressure Chemical Co., had a number-average molecular weight of $M_n = 92\,600 \pm 6\%$ and a weight-average molecular weight of $M_w = 93\,050 \pm 6\%$, and was used as received.

Blend preparation

The copolymers listed in Table I were blended with polystyrene by coprecipitation from dilute toluene solution (3–4 wt. %) into a large excess of methanol (12:1). The precipitates were dried under vacuum at 73 °C for 70 h. The dried samples were then compression molded at 145 °C.

Calorimetric measurements

Differential scanning calorimetry experiments were conducted using a Perkin-Elmer model DSC-2. Samples sizes were approximately 20 mg and a heating rate of 10 °C/min was employed.

RESULTS AND DISCUSSION

Calorimetric studies

The composition of all blends of PS and P(*o*ClS-*p*ClS) investigated was 50/50 by weight. Results of previous investigations[6,12] suggest that the minimum in the cloud point curve is located near or at this composition. We found that P(*o*ClS-*p*ClS) copolymers containing from 71 to 92 mole % *o*ClS were miscible with PS, using the criterion of a single T_g, at the molding temperature of 145 °C. P(*o*ClS-*p*ClS) copolymers containing 62 or less mole % *o*ClS blended with PS displayed two T_g's, indicating an immiscibility for these systems at 145 °C. In these experiments the samples were held at 145 °C for 15 min and then quenched to below T_g. The onset of phase separation in the blends which were miscible at the molding temperature was then determined by annealing at various temperatures. An annealing experiment consisted of heating the blended sample, known to be homogeneous, at a rate of 320 °C/min to the selected annealing temperature and maintaining it at this temperature for 15 min. This period was found by experiment to be sufficiently long to attain phase equilibrium in these samples in the temperature range of interest, but not long enough to induce degradation of either component (as monitored by intrinsic viscosities) at the highest temperature. After annealing samples were rapidly quenched to ambient temperature and subsequently scanned at 10 °C/min. This measurement then revealed either one or two discontinuities in the heat capacity, according to whether or not phase separation had taken place. In a few cases close to the boundary of the miscibility window, the results were somewhat ambiguous. This is partly due to the fact that the glass transition temperatures of the two components differed by only about 30° (Table I).

Figure 1 illustrates examples of the three different cases: a homogeneous sample with a single T_g (curve 1), a phase separated sample with two T_g's (curve 3) and an inter-

TABLE I. Sample characterization.

Sample	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	T_g(°C)
P(*p*ClS)			130
P(*p*ClS-7 *o*ClS)*			126
P(*p*ClS-18 *o*ClS)			126
P(*p*ClS-32 *o*ClS)	~4	~2	124
P(*p*ClS-41 *o*ClS)			121
P(*p*ClS-52 *o*ClS)			121
P(*p*ClS-62 *o*ClS)			122
P(*p*ClS-71 *o*ClS)	4.1	1.9	123
P(*p*ClS-80 *o*ClS)	3.8	1.8	123
P(*p*ClS-86 *o*ClS)	3.6	1.7	126
P(*p*ClS-92 *o*ClS)	3.6	1.8	127
P(*o*ClS)	8.3	2.9	127
PS	0.93	0.926	101

*Numbers indicate mole fractions of *o*-chlorostyrene in the copolymer.

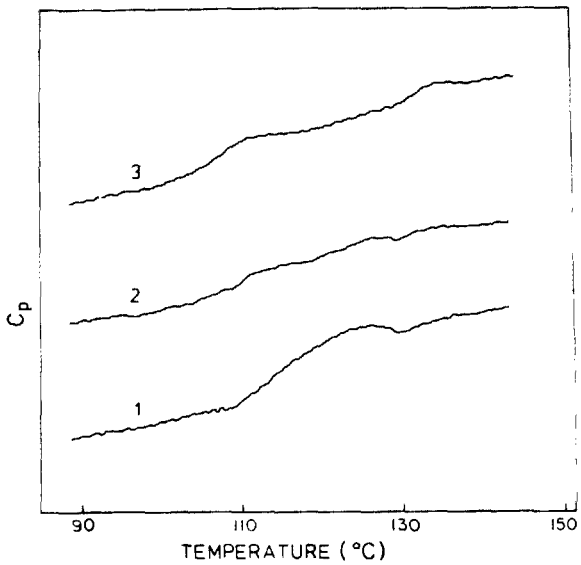

FIG. 1. DSC thermograms of 50/50 wt. % blends of PS and P(*o*ClS-*p*ClS) copolymer containing 85.7 mole % *o*ClS annealed at the following temperatures: (1) 147 °C, (2) 172 °C, and (3) 207 °C.

mediate situation (curve 2). The miscibility window as obtained by these annealing experiments is presented in Fig. 2. Although there is inevitably some difficulty in defining the exact location of the boundary of the miscibility region, two conclusions can be unambiguously drawn. Firstly, the base of the miscibility window at 150 °C extends from approximately 68 to 98 mole % *o*ClS. Secondly, the maximum is located at about 83 mole % *o*ClS and 172 °C.

Numerical analysis

In an earlier publication[2] we presented a simple mean field theory to describe blends of a homopolymer and a random copolymer, or of two random copolymers. The expression for the free energy of mixing for blends of the former type was shown to be identical to the original Flory–Huggins expression provided a parameter χ_{Blend} was introduced which for PS/P(*o*ClS-*p*ClS) takes the form

$$\chi_{\text{Blend}} = x\chi_{\text{S},o\text{ClS}} + (1-x)\chi_{\text{S},p\text{ClS}} - x(1-x)\chi_{o\text{ClS},p\text{ClS}}, \quad (1)$$

where x is the copolymer composition expressed as a volume fraction *o*ClS; the subscripts of the χ parameters are self evident. Miscibility is found if χ_{Blend} is smaller than a critical value of χ given by

$$\chi_{\text{crit}} = \frac{1}{2}\left(\frac{1}{N_1^{1/2}} + \frac{1}{N_2^{1/2}}\right)^2, \quad (2)$$

where N_1 and N_2 are the degrees of polymerization of the respective blend components.

In Ref. 2 we calculated four of the six interaction parameters describing the blends of PPO with P(S-*o*ClS), P(S-*p*ClS), and P(*o*ClS-*p*ClS) at 200 °C from the known miscibility behavior of these systems and from the previously estimated values of 0.005 for $\chi_{\text{S},o\text{ClS}}$, -0.1 for $\chi_{\text{PO,S}}$, and from the calculated value of 0.004 for χ_{crit}. The value for $\chi_{\text{S},o\text{ClS}}$ was based on the observation that PS and P(*o*ClS) are only miscible for a sufficiently low molecular weight of PS.[13,14] Melting point depression[15] and heat of mixing data[16] for PS/PPO provided the value for $\chi_{\text{PO,S}}$, though these results also showed a significant composition dependence in the latter parameter. In this way we obtained, amongst others, the numerical results

$$\chi_{\text{S},p\text{ClS}} = 0.09 \quad \text{and} \quad \chi_{o\text{ClS},p\text{ClS}} = 0.16. \quad (3)$$

From Eq. (1), these results, and a calculated value of 0.002 for χ_{crit}, corresponding to $N_1 = N_2 \simeq 1000$, a miscibility window was predicted extending from about 55 to 95 mole % *o*ClS at 200 °C as discussed above. Consequently, the maximum should occur at approximately 75 mole % *o*ClS. The identification of the calculated miscibility window with the observed one is based on the assumption that the minimum of the cloud point curve is also the critical point. For polydisperse samples this is not true in general[17] but the resulting error may well be negligible compared to other errors in this analysis, as the following discussion demonstrates.

Table II lists the copolymer compositions expressed in volume fractions at the 200 °C miscibility-immiscibility boundaries for blends of PPO with P(*o*ClS-*p*ClS), P(S-*o*ClS), and P(S-*p*ClS). For the PS/P(*o*ClS-*p*ClS) system a miscibility window with a maximum just above 200 °C at about 83 mole % *o*ClS was assumed. This corresponds to an extrapolation to somewhat lower molecular weights than were actually employed and χ_{crit} was accordingly taken to be slightly larger than the value corresponding to the molecular weights listed in Table I. The copolymer compositions at the LCSTs of 200 °C in the blends of PPO/P(S-*o*ClS) and PPO/P(S-*p*ClS) were revised slightly from those used in Ref. 2, and correspond more accurately to refined experimental data. This combination of data provides six equations with six unknowns from which, in principle, the respective χ's may be determined. As it happened the system of six linear equations which should provide independent values for the six unknowns was ill behaved and yielded a linearly dependent system with one degree of freedom. Thus a self-consistent but not absolutely defined set of values for the six χ's was obtained. This is shown in Fig. 3, where the values of five of the interaction parameters are plotted as a function of the sixth, $\chi_{\text{PO,S}}$. Additional information is thus still needed to permit a completely quantitative statement. In our case, we

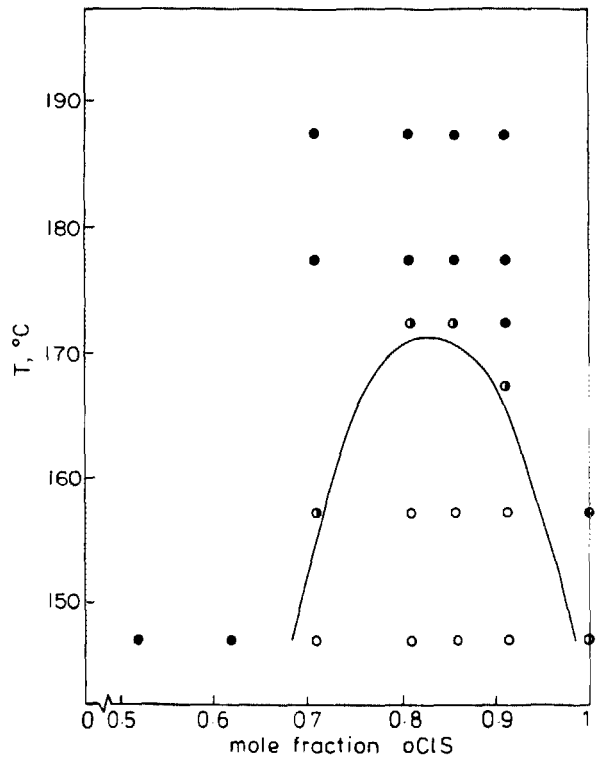

FIG. 2. Miscibility of 50/50 wt. % blends of PS and P(*o*ClS-*p*ClS) as a function of copolymer composition: ○ one phase; ● two phases; ◑ intermediate situation.

TABLE II. Copolymer compositions at phase boundaries.

Blend	Copolymer composition(s_i,x at boundary on 200 °C isotherm	χ_{crit}
PPO/P ($o\text{ClS}_x$-$p\text{ClS}_{1-x}$)	0.32 and 0.78	0.004
PPO/P (S_x-$p\text{ClS}_{1-x}$)	0.195[a]	0.004
PPO/P(S_x-$o\text{ClS}_{1-x}$)	0.23[a]	0.004
PS/P($o\text{ClS}_x$-$p\text{ClS}_{1-x}$)	maximum at $\simeq$0.83	0.002

[a] These values differ slightly from the value of 0.19 used for both of these systems in Ref. 2.

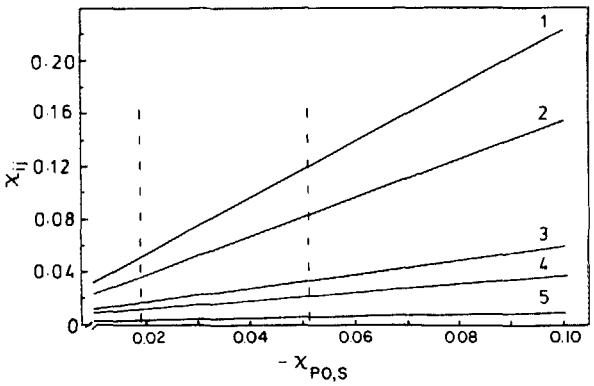

FIG. 3. Interaction parameters as function of $\chi_{PO,S}$: (1) $\chi_{oClS,pClS}$; (2) $\chi_{S,pClS}$; (3) $\chi_{PO,pClS}$; (4) $\chi_{PO,oClS}$; (5) $\chi_{S,oClS}$. Dashed lines define χ_{ij} values consistent with $0.0035 < \chi_{S,oClS} < 0.0055$.

believe that this can again be provided by consideration of the detailed experimental results available for the PS/P(*o*ClS) system.[13,14] The observed phase behavior in this system strongly suggests a value between 0.004 and 0.005 for $\chi_{S,oClS}$. (The results for the PS/PPO system are less clear and also less appropriate in this use, since $\chi_{S,PO}$ varies as function of composition from -0.2 to 0.[15]) Assuming, therefore, as a conservative estimate that $0.0035 < \chi_{S,oClS} < 0.0055$, we can establish a range within which the values of the interaction parameters are located (Fig. 3), realizing at the same time that their *relative* magnitudes are much more precisely determined. In addition, Table III lists the set of χ-parameter values consistent with the choice $\chi_{S,oClS} = 0.005$, used in Ref. 2. Compared to the estimates given in Ref. 2 all the values are slightly smaller in the present, more refined, calculation.

CONCLUDING REMARKS

The results presented in this paper clearly support the validity of the theoretical picture presented previously.[2] Experiments were carried out which largely confirmed the theoretical prediction for the system PS/P(*o*ClS-*p*ClS) for which no information had been available. The results obtained were still insufficient to calculate the temperature behavior of the interaction parameters because of the somewhat unexpected absence of overlap in the temperature regimes of interest for the PS- and PPO-containing blends. However, this method represents perhaps the most readily available technique for measuring segmental polymer-polymer interactions now available. Further, for the system discussed here, containing segments of PPO, PS, halogenated PS, and various copolymeric combinations thereof, the present measurements have suggested that absolute values for the six interaction parameters together with an estimate of their temperature dependence can be obtained by parallel studies using a series of lower molecular weight polystyrene fractions. We estimate the width of the miscibility window at 150 °C should be widened by about 0.1 mole fraction in the copolymer composition axis for blends, for example, containing PS of 5000 daltons and the temperature maximum of the miscibility window concommitantly increased. Such measurements are presently being undertaken.

A second procedure which can yield the necessary number of independent equations is to study miscibility-immiscibility boundaries in appropriate copolymer-copolymer systems. In this case, this would comprise copolymers with one common segment, for example, P(S-*o*CS) and P(S-*p*CS). The utility of this approach is limited only by the requirement that the blend components possess sufficiently differentiated T_g's. This condition can be relaxed if alternative procedures for determining the miscibility-immiscibility boundary, for example, the use of optical and/or neutron scattering, are employed. Such measurements are also presently being carried out.

TABLE III. Segmental interaction parameters at 200 °C.

Segment pair	χ_{ij}	Segment pair	χ_{ij}
PO/S	-0.043 (-0.1)[a]	S/*o*ClS	0.005 (0.005)
PO/*o*ClS	0.02 (0.03)	S/*p*ClS	0.07 (0.09)
PO/*p*ClS	0.03 (0.045)	*o*ClS/*p*ClS	0.10 (0.16)

[a] Values in brackets are taken from Ref. 2.

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